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EXTRAORDINARY REACTIVITY OF THE ETHYLENIC GROUP OF VINYLFERROCENE TOWARD THE ADDITION OF WEAK ACIDS

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IT has been found that vinylferrocene, prepared by the method of Arimoto and Haven,[1] possesses unusual reactivity toward electrophilic reagents, even toward such weakly electrophilic reagents as hydrogen azide and acetic acid. After treatment of 8.3 g of vinylferrocene with 166 ml of a 0.6 N hydrogen azide solution in benzene - absolute acetic acid (1:1) for 3 days at room temperature, the solution was evaporated to dryness, dissolved in Skelly B solvent and chromatographed on Alcoa alumina of reactivity grade 3. Elution with Skelly B solvent gave first 3.6 g (43%) of unreacted vinylferrocene, and, as a second fraction, 1.0 g of a liquid, $\underline{n}_D^{20}$ 1.6110, $\underline{d}_{25}^{25}$ 1.348, which was identified as 1-ferrocenylethyl azide (Calc. for $C_{12}H_{13}N_3Fe$: C, 56.50; H, 5.14; N, 16.47; Found: C, 56.77; H, 5.01; N, 16.72) by conversion to the known 1-ferrocenylethylamine[2] under conditions of catalytic hydrogenation, by preparation of the same azide in 57% yield from 1-ferrocenyl-

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[1] F. S. Arimoto and A. C. Haven, Jr., J. Amer. Chem. Soc. 77, 6295 (1955).

[2] P. J. Graham, R. V. Lindsey, G. W. Parshall, M. L. Peterson and G. M. Whitman, J. Amer. Chem. Soc. 79, 3416 (1957).

ethyl alcohol by reaction with hydrogen azide under the same conditions as used in the addition of the acid to vinylferrocene, and by the presence of an infrared absorption peak in carbon disulfide solution at 4.80 μ, characteristic of the azido group. Further elution of the material on the alumina column with Skelly B-chloroform (9:1) yielded of 0.2 g of an unknown liquid (Found: C, 51.04; H, 4.51; N, 25.00; Fe, 19.93), which showed in carbon disulfide solution the presence of a strong absorption peak at 4.82 μ. A final elution with Skelly B-chloroform (4:1) afforded two additional fractions, the first of which amounted to 0.3 g and was identified as acetylferrocene. The second fraction, 3.10 g, was shown to be 1-ferrocenylethyl alcohol, formed by addition of acetic acid to the ethylenic group of vinylferrocene, followed by hydrolysis on the alumina column of the resulting acetate. In independent experiments, the alcohol was prepared in high yield by addition of acetic acid to the olefin in benzene-acetic acid (1:1) and subsequent chromatographic treatment of the product.

There is good reason to believe that the acetylferrocene obtained in the chromatographic separation arose from decomposition of 1-ferrocenylethyl azide to the corresponding imine, followed by hydrolysis of the latter compound. Whenever the pure azide is allowed to stand for some time and then re-chromatographed, acetylferrocene is obtained in addition to the azide.

The facile addition of both hydrogen azide and acetic acid to vinylferrocene appears to be without parallel in reactions of monosubstituted ethylenes. Since it is wll understood that the addition of acids to ethylenic groups proceeds by the initial addition of a proton, the results described in this Letter clearly imply that the carbonium ion Ferr-$\overset{+}{C}H$-CH_3, or a related transition ion having a protonated double bond, is formed much more rapidly than the analogous transition ions which would have to arise from other monosubstituted ethylenes in similar addition reactions. The conclusion that the carbonium ion Ferr-$\overset{+}{C}H-CH_3$ possesses unusual stabilizing features has also been reached recently by Richards,[3] who observed that 1-ferrocenylethyl acetate undergoes rapid solvolysis in 80% acetone at 30° by the $B_{AL}1$ mechanism.

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[3] J. H. Richards, Abstracts of Papers Presented at the 135th National Meeting of the American Chemical Society, Boston, April 5-10, 1959. pp. 87-90.